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Synthesis and Isolation of σ-Bonded Fullerene Metal Derivatives from Reactions of Fullerene Dianion $C_{60}{}^{2-}$ with Organometal Halides

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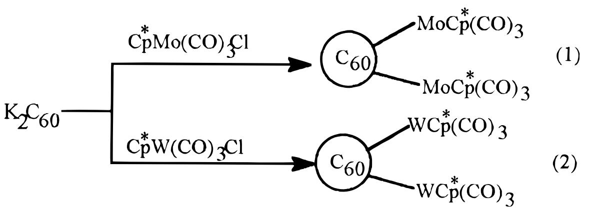
ABSTRACT



$(Cp^{*} = \eta^5\text{-}C_5H_4CO_2C_2H_5;\ \eta^5\text{-}C_5H_4CO_2CH_3)$

Two novel fullerene derivatives (μ-C_{60})$Mo_2(CO)_6$(η^5-$C_5H_4CO_2Et)_2$ (1) and (μ-C_{60})$W_2(CO)_6$(η^5-$C_5H_4CO_2Me)_2$ (2) were isolated from reactions of a tetrahydrofuran (THF) solution of dianion $C_{60}{}^{2-}$, derived from C_{60} and potassium as well as α-methylnaphthalene, in situ with (η^5-$C_5H_4CO_2$Et)$Mo(CO)_3Cl$ and (η^5-$C_5H_4CO_2Me)W(CO)_3Cl$, respectively (Scheme 1). The new complexes, in which the organometallic groups are attached at the 1,4-positions of C_{60} via assigned Mo–C(C_{60}) σ-bonds, were characterized by elemental analysis and spectroscopic methods.

Organometallic fullerene C_{60} derivatives containing π-bonds between C_{60} skeletons and transition metal centers have received considerable attention since their preparation was reported.[1−8] Though one noteworthy example is provided by Shaplepy's pioneering studies on the rhenylation of C_{60}, cases in which fullerene C_{60} attaches to a transition metal center in the form of a Mo−C(C_{60}) σ-bond are rare.[9−11] The σ-bonded species is of further interest with regard to the synthesis of new fullerene derivatives. We have recently initiated a project to investigate the properties of dianion $C_{60}{}^{2-}$ [12] and to synthesize the title complexes. We report our latest results in this Letter.

Under a highly prepurified argon atmosphere, treatment of a THF solution of K_2C_{60} at 0 °C with organometallic halides resulted in an obvious color change from deep red-brown to emerald-green, and some black insoluble material was produced. After filtration, removal of the solvent, and purification with silical gel column chromatography eluting

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(1) Fagan, P. J.; Calabrese, J. C.; Malone, B. *Science* **1991**, *252*, 1160.

(2) Fagan, P. J.; Calabrese, J. C.; Malone, B. *J. Am. Chem. Soc.* **1991**, *113*, 9408.

(3) Bashilov, V. V.; Petrovskii, P. V.; Sokolov, V. I.; Lindernan, S. V.; Guzey, I. A.; Struchov, Y. I. *Organometallics* **1993**, *12*, 991.

(4) Hus, H. F.; Shapley, J. R. *J. Am. Chem. Soc.* **1996**, *118*, 1192.

(5) Lee, K.; Hsu, H. F.; Shapley, J. R. *Organometallics* **1997**, *16*, 3876.

(6) (a) Shapley, J. R.; Du, Y.; Hsu, H.-F.; Way, J. J. *Proc.-Electrochem. Soc.* **1994**, *24*, 1255. (b) Song, L.-C.; Zhu, Y.-H.; Hu, Q.-M. *Polyhedron* **1997**, *16*, 2141. (c) Song, L.-C.; Zhu, Y.-H.; Hu, Q.-M., *Polyhedron* **1998**, *17*, 469.

(7) Iglesias, M.; Santos, A. *Inorg. Chim. Acta* **1996**, *248*, 67.

(8) Tang, K.; Zheng, S.; Jin, X.; Zeng, H.; Gu, Z.; Zhou, X.; Tang, Y. *J. Chem. Soc., Dalton Trans.* **1997**, 3585.

(9) Zhang, S.; Brown, T. L.; Du, Y.; Shapley, J. R. *J. Am. Chem. Soc.* **1993**, *115*, 6705.

(10) Ballenweg, S.; Gleiter, R.; Kratschmer, W. *Tetrahedron. Lett.* **1993**, *34* , 3737.

(11) Fullagar, W. K.; Reynolds, P. A.; White, J. W. *Solid state commun.* **1997**, *104*, 23.

(12) Cai, Y.-F.; Cheng, J.; Huang, Z.-E.; Shao, Q.-F. *Kexue Tongbao* **1995**, *40*, 1263.

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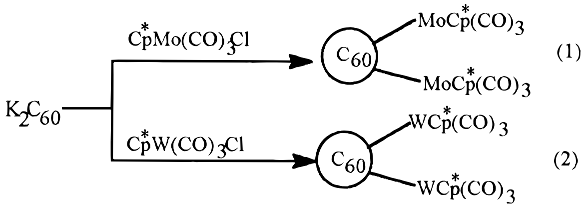
with a toluene/hexane mixture, as well as recrystallization from CS_2/hexane, the emerald-green powder products of **1** and **2** were isolated.[13−15] Apparently, the α-methylnaphthalene used in this preparation first served as an electron acceptor of potassium and then as an electron donor to transfer the electron to C_{60}. Since α-methylnaphthalene is relatively inert and can be easily removed, the K_2C_{60} solution prepared might be utilized in situ to synthesize various C_{60} derivatives conveniently. The formation of **1** and **2** proceeds via a nucleophilic substitution reaction of the anion C_{60}^{2-} with organometallic halides as shown in Scheme 1. Both **1** and **2** are relatively stable in toluene below ambient temperature, but in boiling toluene, they decompose to give C_{60} and some other insoluble brown materials, even under the protection of highly purified nitrogen. In addition, **2** decayed slower than **1** under similar conditions. This suggests that the tungsten derivative of C_{60} is more stable than the molybdenum derivative.

Scheme 1



($Cp^* = \eta^5\text{-}C_5H_4CO_2C_2H_5$; $\eta^5\text{-}C_5H_4CO_2CH_3$)

Besides C_{60} ion peaks, the FAB-MS spectra of **1** and **2** both display molecular ion peak clusters at $m/z = 1354$ and 1502, respectively. The ^1H NMR spectra of **1** and **2** consist of substituted Cp signals at 5.1−6.0 ppm as triplets,[16] ethyl signals at ca. 1.3 ppm as triplets and ca. 4.3 ppm as quartets, and a methyl signal at ca. 3.9 ppm. The ^{13}C NMR spectra of **1** and **2**, both determined in $CDCl_3$ solvent, display 32 resonances for the C_{60} skeleton. Of the 32, one C_{60} carbon atom resonates at about 61 ppm; this suggests a C_s symmetry for molecules of **1** and **2**. The ^{13}C NMR spectrum of compound **1** is shown in Figure 1. The near-IR spectra of **1** and **2** show four absorption bands from 1451 to 520 cm^{-1} for C_{60} ligands and absorption bands from 2057 to 1922 cm^{-1} for terminal carbonyls. The far-IR spectra of **1** and **2** both exhibit one strong band around 160 cm^{-1} (Figure 2). The UV−vis spectra of **1** and **2** are similar to that of free C_{60} in peak shapes as are many other C_{60} derivatives.

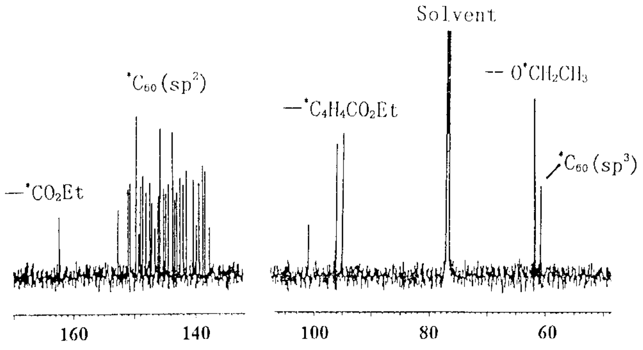


Figure 1. ^{13}C NMR spectrum of compound **1**.

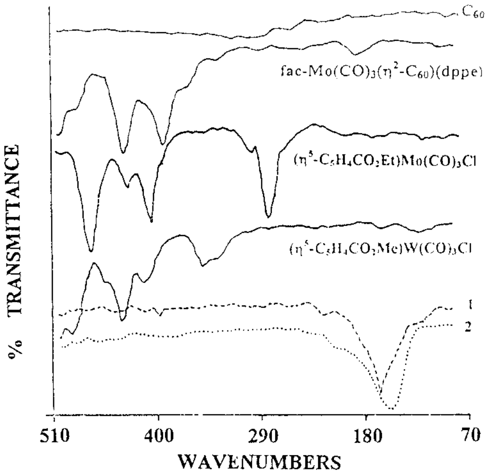


Figure 2. Far-IR spectra of C_{60}, $(\eta^5\text{-}C_5H_4CO_2Et)Mo(CO)_3Cl$, $(\eta^5\text{-}C_5H_4CO_2Me)W(CO)_3Cl$, $(\mu\text{-}C_{60})Mo_2(CO)_6(\eta^5\text{-}C_5H_4CO_2Et)_2$, $(\mu\text{-}C_{60})W_2(CO)_6(\eta^5\text{-}C_5H_4CO_2Me)_2$, and fac-$Mo(CO)_3(\eta^2\text{-}C_{60})$(dppe).

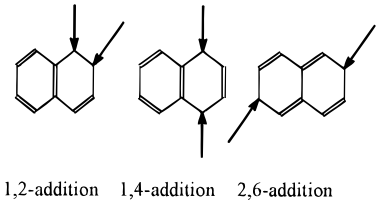


Figure 3. Different bisaddition patterns.

It has been reported that dimethylation of C_{60} gives two main regioselective isomers, $1,2\text{-}Me_2C_{60}$ and $1,4\text{-}Me_2C_{60}$ (Figure 3), which is consistent with the results of semiempirical calculations.[17] In the case of bisadduct **1**, the ^{13}C NMR spectrum displays 32 signals for the C_{60} carbon atoms, supporting C_s symmetry: 31 resonanate at low field and one at high field, 22 resonances of intensity 2, four of intensity 1, and three of intensity 4. Thus, the number of carbon atoms adds up to 60. Of the 32, one C_{60} carbon atom resonates at 60.7 ppm. This strongly supports 1,4-addition and excludes the possibility of 1,2-addition and 2,6-addition patterns, which provide C_{2v} and C_2 symmetry, respectively. The far-IR spectrum of **1** does show a strong absorption at ∼160 cm^{-1}, which is distinctively different from the far-IR spectra of free C_{60}, $(\eta^5\text{-}C_5H_4CO_2Et)Mo(CO)_3Cl$, $(\eta^5\text{-}C_5H_4CO_2Me)W(CO)_3Cl$, and the π-bonded fullerene organomolybdenum derivative fac-$Mo(CO)_3(\eta^2\text{-}C_{60})(dppe)$.[6c] This confirms the formation of a new bond between C_{60} and the organomolybdenum group, which is different from the π-bond of Mo−C(C_{60}). According to our knowledge, there is no previous report on the appearance of the sp^3 carbon resonance in the C_{60} cage of a π-bonded fullerene organomolybdenum compound in ^{13}C NMR spectra except Jin's studies on the W and Mo complexes of C_{60} at $\delta = 77$ ppm, which is actually difficult to attribute to C_{60}, dbm, or $CDCl_3$.[8] The ^{13}C NMR spectrum of **1** clearly shows one sp^3 carbon signal for C_{60}. On the basis of all the spectroscopic results, we assign compound **1** to the 1,4-isomer via C(C_{60})−Mo σ-bonds. Compound **2** has spectroscopic results and a structure similar to that of **1**. An exact assignment of bond type cannot be made at this time and must await X-ray structural determinations.

We have found a convenient route for the synthesis of σ-bonded fullerene transition metal derivatives through the nucleophilic substitution reactions of $C_{60}{}^{2-}$ with organometallic halides. Further studies such as reactions of $C_{60}{}^{2-}$ with inorganic halides MCl_2 (M = Zn, Hg) are in progress.

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Supporting Information Available: ^{1}H NMR, ^{13}C NMR, near-IR, far-IR, FAB-MS, and UV−vis spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) Syntheses and spectral data of compounds **1** and **2.** Under a highly prepurified argon atmosphere, a dry 100 mL Schlenk flask was charged with 80 mg (0.11 mmol) of C_{60}, 9 mg (0.23 mmol) of K, 50 mL of THF, and 1.0 mL of α-methylnaphthalene. The suspention was chilled to 0 °C and stirred for 4−5 h to form a red-brown solution. To this solution was added 78 mg (0.22 mmol) of $(\eta^5\text{-}C_5H_4CO_2C_2H_5)Mo(CO)_3Cl$,[14] and the solution was stirred at 0 °C for about 6 h to produce an emerald-green solution. The mixture was allowed to warm to room temperature spontaneously and filtered to leave a black residue (undetected, owing to its very small quantity). After removal of solvent from the filtrate in vacuo and washing with 40 mL of hexane/toluene (6/1) to remove any unreacted $(\eta^5\text{-}C_5H_4CO_2C_2H_5)Mo(CO)_3Cl$ and α-methylnaphthalene, the residue was extracted into 15 mL of toluene and passed through a 2 × 40 cm column of silical gel eluting with toluene/hexane (1/2). The evaporated residue from the major second band was recrystallized by extraction into 15 mL of CS_2 followed by addition of 60 mL of hexane. A green solid was filtered off and washed with 40 mL of hexane to yield 82 mg of **1** (55%). Mp: 160−162°C (dec). Anal. Calcd for $(\mu\text{-}C_{60})Mo_2(CO)_6(\eta^5\text{-}C_5H_4CO_2Et)_2$: C, 72.69; H, 1.34; Mo, 14.16. Found: C, 72.57; H, 1.29; Mo, 14.06. FAB-MS, *m*/*z*: 1354 (molecular ion peak cluster), 720 ($C_{60}{}^+$). ^{1}H NMR (200 MHz, $CDCl_3$): 1.29 (t, 6H, $2CH_3$), 4.28 (q, 4H, $2CH_2O$), 5.85 (t, 4H, H^3, H^4), 6.08 (t, 4H, H^2, H^5) ppm. Near-IR (KBr, disk), $\nu_{C\equiv O}$: 2053 (vs), 1970 (vs), 1966 (vs) cm^{-1}. UV−vis (toluene, 1.73×10^{-5}M), λ_{max} (log ϵ): 283.2 (1.44), 336.0 (1.17), 406.2 (0.15) nm. ^{13}C NMR (200 MHz, $CDCl_3$): δ 152.60 (2C), 151.14 (2C), 150.70 (2C), 149.90 (4C), 149.30 (1C), 149.02 (2C), 148.60 (2C), 148.13 (2C), 147.23 (2C), 147.06 (2C), 146.63 (1C), 146.02 (2C), 145.87 (4C), 145.01 (2C), 144.93 (2C), 144.12 (2C), 143.83 (4C), 143.56 (2C), 143.04 (2C), 142.23 (2C), 141.97 (2C), 141.15 (2C), 140.09 (2C), 139.80 (1C), 139.15 (2C), 138.84 (2C), 138.12 (2C), 137.41 (1C); 60.73 (2C, sp^3) ppm. With a process similar to the preparation of **1**, from the reaction of K_2C_{60} with $(\eta^5\text{-}C_5H_4CO_2CH_3)W(CO)_3Cl$,[15] **2** was synthesized and isolated as a green solid in 57% yield. Mp: 179−181°C (dec). Anal. Calcd for $(\mu\text{-}C_{60})W_2(CO)_6(\eta^5\text{-}C_5H_4CO_2Me)_2$: C, 63.94; H, 0.94; W, 24.47. Found: C, 63.62; H, 1.03; W, 24.15. FAB-MS, *m*/*z*: 1502 (molecular ion peak cluster), 722 ($C_{60}{}^+ + 2$). ^{1}H NMR (200 MHz, $CDCl_3$): 3.87 (s, 6H, $2CH_3$), 5.11 (t, 4H, H^3, H^4), 5.98 (t, 4H, H^2, H^5) ppm. Near-IR (KBr, disk), $\nu_{C\equiv O}$: 1997 (vs), 1952 (vs), 1922 (vs) cm^{-1}. UV−vis (toluene, 1.64×10^{-5}M), λ_{max} (log ϵ): 283.0 (1.38), 335.4 (1.13), 405.7 (0.23) nm. ^{13}C NMR (200 MHz, $CDCl_3$): δ 152.59 (1C), 151.75 (2C), 151.22 (2C), 150.79 (2C), 150.35 (2C), 150.02 (2C), 149.73 (2C), 149.54 (2C), 149.47 (2C), 149.06 (2C), 148.53 (2C), 148.03 (1C), 147.60 (2C), 147.11 (2C), 146.65 (2C), 146.30 (4C), 146.01 (1C), 145.48 (4C), 145.07 (2C), 144.50 (2C), 143.69 (2C), 143.09 (4C), 142.76 (2C), 142.12 (2C), 141.59 (4C), 140.82 (1C), 139.69 (2C); 62.03 (2C, sp^3) ppm.

(14) Song, L.-C.; Dong, Q.; Hu, Q.-M. *Acta Chim. Sin.* **1991**, *49*, 1129.

(15) Song, L.-C. Dong, Q.; Hu, Q.-M. *Youji Huaxue* **1992**, *12*, 35.

(16) Macomber, D.W.; Rausch, M. D. *J. Organomet. Chem.* **1983**, *258*, 331.

(17) Caron, C.; Subramanian, R.; D′Souza, F.; Kim, J.; Kuter, W.; Jones, M. T.; Kadish, K. M. *J. Am. Chem. Soc.* **1993,** *115*, 8505.